

# Purification of Oxyfuel-Derived CO<sub>2</sub> for Sequestration or EOR

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## Abstract

Certain CO<sub>2</sub> capture processes, particularly Oxyfuel combustion in a pulverised fuel coal-fired power station, produce a raw CO<sub>2</sub> product containing contaminants such as water vapour, and oxygen, nitrogen and argon derived from the excess oxygen, impurities in the oxygen used, and any air leakage into the system. There are also acid gases present, such as SO<sub>3</sub>, SO<sub>2</sub>, HCl and NO<sub>x</sub> produced as products of combustion. These acidic impurities will need to be removed from the CO<sub>2</sub> stream before it is introduced into the pipeline to prevent corrosion and comply with possible regulations. There may also be other stringent requirements on purity, particularly for applications such as enhanced oil recovery. In this paper we present an integrated process for CO<sub>2</sub> compression and simultaneous purification to produce CO<sub>2</sub> product streams at purities up to essentially pure CO<sub>2</sub>.

**Keywords:** CO<sub>2</sub> Purification, SO<sub>2</sub>, NO<sub>x</sub>, oxyfuel

## Introduction

Oxyfuel combustion in a pulverised coal-fired power station produces a raw CO<sub>2</sub> product containing contaminants such as water vapour, and oxygen, nitrogen and argon derived from the excess oxygen, impurities in the oxygen used, and any air leakage into the system. There are also acid gases present, such as SO<sub>3</sub>, SO<sub>2</sub>, HCl and NO<sub>x</sub> produced as products of combustion. These acidic impurities will need to be removed from the CO<sub>2</sub> stream before it is introduced into the pipeline to prevent corrosion and comply with possible regulations. There may also be stringent requirements on purity, particularly for applications such as enhanced oil recovery.

Direct contact water scrubbing is used to cool the net flue gas product from the power boiler, condense water vapour present in the flue gas, and remove residual ash particles and highly soluble HCl and SO<sub>3</sub> before further compression and purification. The CO<sub>2</sub> must be purified to meet the requirements of the pipeline transportation system and the constraints of the proposed storage site, such as a deep saline aquifer or a hydrocarbon formation where the CO<sub>2</sub> could be used for enhanced oil recovery. This would normally involve inerts removal to avoid increasing the critical pressure of CO<sub>2</sub> in the pipeline and possible two-phase flow developing, leading to CO<sub>2</sub> purities of around 95-98% minimum.

This paper presents a mechanism for the removal of SO<sub>2</sub>, NO<sub>x</sub> and mercury from the raw CO<sub>2</sub> as it is compressed, prior to inerts removal. The requirements of enhanced oil recovery affect the purification of CO<sub>2</sub> requiring removal of oxygen down to around 10 ppmv. Low temperature inerts removal from crude CO<sub>2</sub> using phase separation has been described previously by the authors [1]. It results typically in an oxygen content of 1mol% and a total inerts level of 2-5 mol%.

## Current Technology For Oxyfuel CO<sub>2</sub> Purification

The process for purifying raw CO<sub>2</sub> from oxyfuel combustion of pulverised coal is shown in Figure 1 and Figure 2. Figure 1 shows the raw CO<sub>2</sub> cooling and compression to a processing pressure of about 30 bar and Figure 2 shows the low temperature purification process. The impure CO<sub>2</sub> from the power boiler is cooled by direct contact water scrubbing in a packed tower, C101, to condense water vapour, remove traces of ash and dissolve soluble gases such as SO<sub>3</sub> and HCl. The circulating water system used for scrubbing is cooled by indirect heat transfer with a cooling water stream in E101 and a filtration system removes any ash present. The net condensed water together with the soluble impurities is sent to a water treatment system for further purification. Very little SO<sub>2</sub> or NO<sub>x</sub> is removed in this water scrubbing process. The ambient temperature CO<sub>2</sub> at atmospheric pressure is compressed to an intermediate pressure of about 30 bar in an axial/centrifugal flow adiabatic compressor K101 and K102. The heat of compression is recovered for boiler feedwater heating, in E102, and condensate preheating, in E103, in the boiler steam system, reducing the requirement for steam preheating. E104 and E106 are final coolers using cooling water. E104 and E106 are final coolers using cooling water.

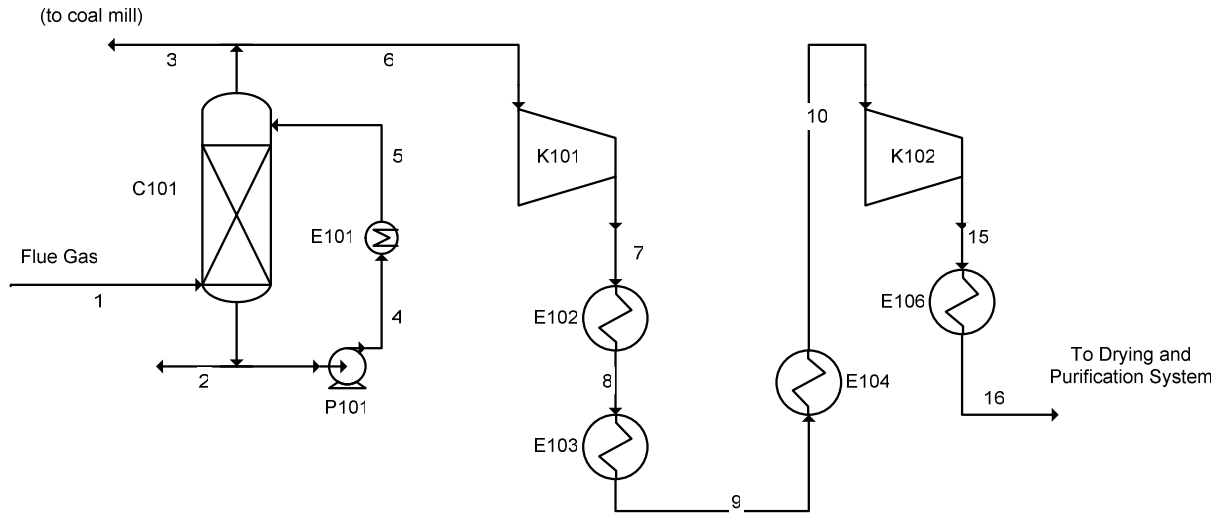


Figure 1: Raw CO<sub>2</sub> Cooling and Compression to 30 bar

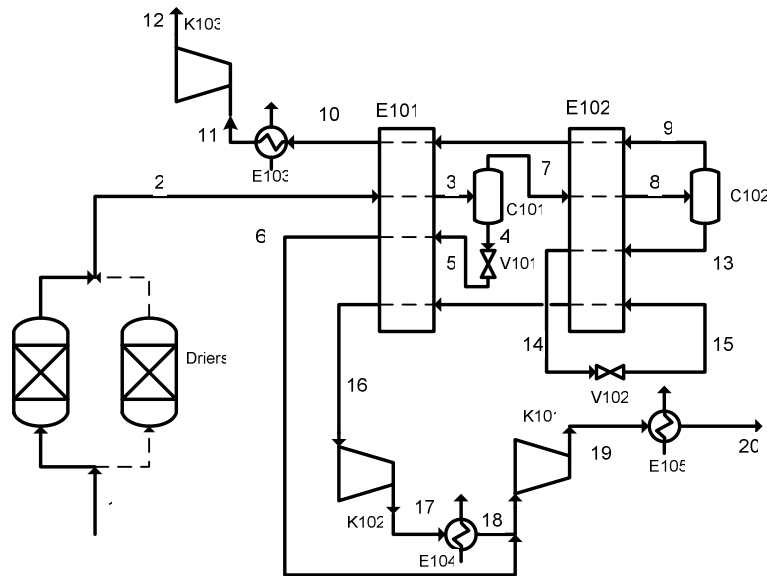


Figure 2: CO<sub>2</sub> Inerts Removal and Compression

The impure 30 bar CO<sub>2</sub> is then dried in a dual-bed thermally regenerated desiccant drier. Oxygen, nitrogen and argon are removed from the CO<sub>2</sub> by low temperature processing, shown in Figure 2. The impure CO<sub>2</sub> is cooled in E101 and E102 against evaporating lower pressure liquid CO<sub>2</sub> streams to a temperature of -55°C, close to its triple point, which reduces the partial pressure of CO<sub>2</sub> in the uncondensed gas stream to about 5 bar, corresponding to a typical concentration of approximately 20-25mol% CO<sub>2</sub>. The inerts stream leaving the cold equipment at about 30 bar is further heated and power is recovered from the stream using a power turbine. The purified CO<sub>2</sub> streams leaving the cold equipment are compressed in a second stage of CO<sub>2</sub> compression which is adiabatic with heat recovered to the boiler steam system in E105. Adiabatic compression ensures better aerodynamic characteristics in the CO<sub>2</sub> compression system near the critical points and confines the rapid density change to the aftercooler.

Once the net flue gas is cooled by direct contact with water, as in Figure 1, the raw CO<sub>2</sub> composition entering the CO<sub>2</sub> compressor is then typically as shown in column 1 of Table 1 [2]. After CO<sub>2</sub> purification as described above, the CO<sub>2</sub> product will have the composition shown in column 2 of Table 1. Although some of the NO<sub>x</sub>, N<sub>2</sub>, O<sub>2</sub> and Ar are removed, all of the SO<sub>2</sub> was believed to leave with the CO<sub>2</sub>. We will now discuss why we no longer believe that to be the case and that the correct compositions in Table 1 column 3 are more typical of the CO<sub>2</sub> purities one can expect from the process in Figure 1 and Figure 2.

**Table 1: Raw and Product CO<sub>2</sub> Compositions from basic oxyfuel process**

	Raw Flue Gas @ 35°C, 1.02 bara mol%	CO <sub>2</sub> Product @ 35°C, 110 bar mol% <b>Prior Art</b>	CO <sub>2</sub> Product @ 35°C, 110 bar mol% <b>Corrected</b>
CO <sub>2</sub>	71.5	95.8	96.3
N <sub>2</sub>	14.3	2.0	2.0
O <sub>2</sub>	5.9	1.1	1.1
Ar	2.3	0.6	0.6
SO <sub>2</sub>	0.4	0.5	0.0
NO	0.04	0.01	0.0
H <sub>2</sub> O	5.6	0.0	0.0

### NO<sub>x</sub>, SO<sub>x</sub> and Hg Emissions in Oxyfuel Combustion

Little attention has been given to the removal of NO<sub>x</sub> and mercury compounds in oxyfuel combustion system. In the low temperature inerts removal system no detailed analysis has yet been presented on the behaviour of NO and NO<sub>2</sub> in the separation train. Indeed, in previously published work the assumption has been that most of the NO present in the CO<sub>2</sub> feed would leave with the inert gas while NO<sub>2</sub> would leave with the liquid CO<sub>2</sub>. Mercury could be distributed between the condensed water produced in the compression process and the CO<sub>2</sub> product, although one would assume that the desiccant drier would also catch some of this mercury. Finally, it has generally been accepted that the SO<sub>2</sub> present in the raw CO<sub>2</sub> stream will leave with the CO<sub>2</sub>. This solution allows co-disposal of SO<sub>2</sub> with CO<sub>2</sub>, which may or may not be acceptable/allowed under future CO<sub>2</sub> capture regulations.

Our aim in undertaking this research was to determine a method of producing NO<sub>x</sub>-free, SO<sub>2</sub>-free, Hg-free and O<sub>2</sub>-free CO<sub>2</sub> to meet all possible specifications of CO<sub>2</sub>, for geological disposal and enhanced

oil recovery applications. Of course, in oxyfuel combustion it is possible to use the same NO<sub>x</sub>, SO<sub>x</sub> and Hg removal technology as used and required by air-fired combustion. We aim to show that this is not required for oxyfuel combustion.

### NO<sub>x</sub>, SO<sub>x</sub> and Hg Removal in Oxyfuel Combustion

To improve the purity of the CO<sub>2</sub> we could remove the NO<sub>2</sub> and SO<sub>2</sub> together in a distillation step, integrated into the inerts removal process. This is discussed in prior publications [2,3]. NO<sub>x</sub> from the boiler is mostly produced as NO. To remove NO from the CO<sub>2</sub>, NO would have to convert to NO<sub>2</sub> and be distilled from the system. Conversion of NO to NO<sub>2</sub>:



has been studied by many authors in the 20<sup>th</sup> century and their results are reviewed in reference [4]. At the high temperatures at which NO<sub>x</sub> is formed, the equilibrium dictates that mostly NO will be formed. At low temperature, the equilibrium of Equation 1 is strongly in favour of NO<sub>2</sub> production rather than NO, however at low pressure the rate of the Equation 1 is low and so, in an air fired boiler without CO<sub>2</sub> capture or NO<sub>x</sub> removal, the main emission would be NO. Therefore, a method of increasing the conversion of NO to NO<sub>2</sub> was required.

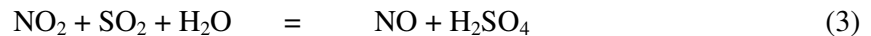
The rate of Equation 1 is slow but speeds up with *decreasing* temperature and increasing pressure and the reaction is a third order reaction:

$$d[\text{NO}_2]/dt = 2k [\text{NO}]^2 \cdot [\text{O}_2] \quad (2)$$

where k, in l<sup>2</sup> mol<sup>-2</sup> s<sup>-1</sup>, is 1200 x 10<sup>230/T</sup> [3] where T is in kelvin. Since the rate is therefore proportional to pressure to the 3<sup>rd</sup> power, this reaction rate is likely become significant at higher pressures and low temperatures. The first such place in the oxyfuel purification process is after compression to 15 bar point in the compression train, i.e. as the compressed 15 bar raw CO<sub>2</sub> is cooled in exchangers E102, E103 and E104 in Figure 1.

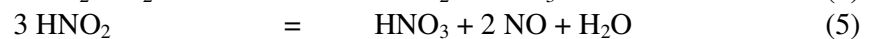
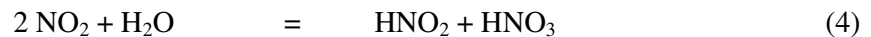
Therefore, we are confident that at the 15 bar point in the CO<sub>2</sub> compression system, the rate of Equation 1 will have increased sufficiently for it to require only a few seconds to reach equilibrium and convert most of the NO to NO<sub>2</sub> especially since there is plenty of oxygen in the raw CO<sub>2</sub> stream, due to the excess oxygen required for combustion.

The second reaction of significance at this point is the reaction of NO<sub>2</sub> with SO<sub>2</sub> to form sulphuric acid, commonly referred to as the lead chamber process for the manufacture of sulphuric acid:



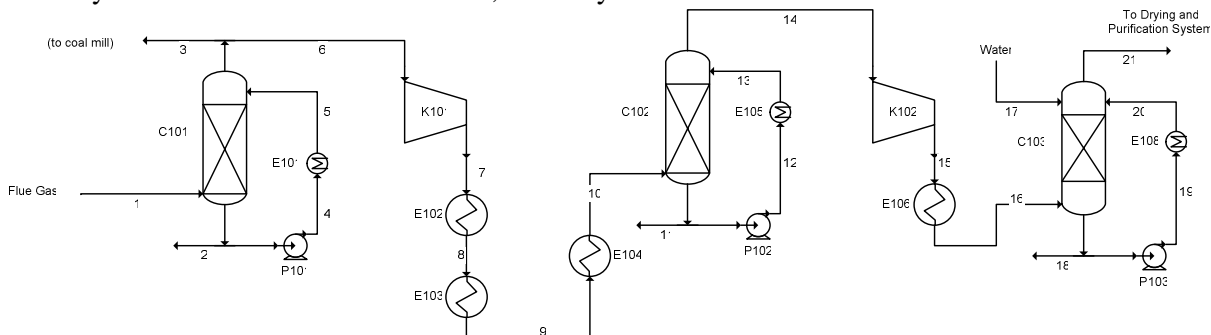
This reaction is known to be fast and so is considered to be equilibrium limited.

Once all of the SO<sub>2</sub> has been removed by Equations 1 and 3, NO<sub>2</sub> will be converted to nitric acid by the well understood process nitric acid process:



with the NO formed in Equations 3 and 5 being reconverted to NO<sub>2</sub> by Equation 1.

These reactions give a path-way for SO<sub>2</sub> to be removed as H<sub>2</sub>SO<sub>4</sub> and NO and NO<sub>2</sub> to be removed as HNO<sub>3</sub>. Any elemental mercury or mercury compounds present in the gaseous carbon dioxide will also be removed as mercury will be converted to mercuric nitrate since mercury compounds react readily with nitric acid. Typical nitric acid concentrations in the process will be sufficient to remove all mercury from the carbon dioxide stream, either by reaction or dissolution.



**Figure 3: Raw Oxyfuel CO<sub>2</sub> Compression with Integrated SO<sub>x</sub> and NO<sub>x</sub> removal**

To allow the reactions so far presented to proceed so as to remove SO<sub>2</sub>, NO and NO<sub>2</sub> from the process, residence time and contact with water must be introduced after compression of the raw CO<sub>2</sub> as shown in Figure 3. It is mentioned above that, after adiabatic compression to 15 bar the CO<sub>2</sub> is cooled by preheating Boiler Feed Water (BFW) and condensate. Final cooling is with cooling water. At this point condensate will be removed. At this point holdup is added to the process, by, for instance, the use of a contacting column with pumped-around liquid condensate. A holdup of only a few seconds was found to allow time for all of the SO<sub>2</sub> to be removed as H<sub>2</sub>SO<sub>4</sub>. The contactors allow intimate mixing of water with SO<sub>3</sub> and then with NO<sub>2</sub> to remove these components from the gas continuously thus allowing reactions to proceed until all SO<sub>2</sub> and the bulk of the NO is removed. No HNO<sub>2</sub> or HNO<sub>3</sub> will be formed until all of the SO<sub>2</sub> has been consumed. NO<sub>2</sub> formed by the slow Equation 1 will be consumed by the fast reaction in Equation 3 before the slow reaction in Equation 4 can produce HNO<sub>2</sub> or HNO<sub>3</sub>.

In this example, the SO<sub>2</sub>-free CO<sub>2</sub> is then compressed to 30 bar before being dried and inerts removed. This 30 bar point is considered the ideal location to remove the NO and NO<sub>2</sub> from the process. A similar process as at 15 bar adds another few seconds of holdup to the process. Around 90% of the NO<sub>x</sub> and all of the SO<sub>2</sub> can be removed in this way from the CO<sub>2</sub> before inerts removal.

### Oxygen Removal from CO<sub>2</sub>

The purity of CO<sub>2</sub> required for enhanced oil recovery is greater than that required for other geological storage sinks due the requirement to minimise oxygen content as this would react with the hydrocarbons within the oil field. This adds complication to the purification of CO<sub>2</sub> from oxyfuel applications as there may be around 1mol% oxygen in the captured CO<sub>2</sub> due to the excess oxygen from combustion. This oxygen could be removed by using a fuel rich combustor, or using a catalytic combustor, to consume the oxygen present in the CO<sub>2</sub> before inerts removal. The route we have chosen though is to modify the flowsheet in Figure 2 to incorporate distillation of the liquid CO<sub>2</sub> to remove oxygen. This allows us to reach purities of 10ppm O<sub>2</sub> in the CO<sub>2</sub> without adding other impurities that might be created by fuel rich combustion.

## The Power, Recovery and Purity Trade-off in CO<sub>2</sub> purification

Table 2 shows three different options for CO<sub>2</sub> purification from an oxyfuel-fired coal combustion system. Actual powers will depend upon the type of coal burned and the amount of air inleakage there is into the boiler, since this will dictate the level of inerts that must be removed from the raw CO<sub>2</sub>, together with issues such as cooling water temperature. However, the numbers within Table 2 are consistent. What one can see is that low purity CO<sub>2</sub>, as produced by the flowsheet in Figure 2, requires the lowest power and gives the highest capture of the contained CO<sub>2</sub>. Increasing the purity of the CO<sub>2</sub> using an alteration to Figure 2 described in [2] decreases recovery by 2% with a 1% reduction in power, so overall a reduction in capture efficiency. To reach the higher purities required by EOR leads to around 5% increase in power. Therefore, one can say that the extra penalty of achieving EOR-grade CO<sub>2</sub> from oxyfuel-fired coal combustion is both feasible and tolerable as an extra energy penalty.

**Table 2: Power, Recovery and Purity in Oxyfuel CO<sub>2</sub> purification**

CO <sub>2</sub> Purity	Oxygen Content	CO <sub>2</sub> Recovery	Power <sup>1</sup> from 1 to 110 bar, kWhr/tonne CO <sub>2</sub> Captured
95.9 mol%	0.9 mol%	89.0 %	168.5
98 mol%	0.4 mol%	87.0 %	166.5
99.97 mol%	10 ppmv	87.4 %	177.1

## Conclusions

The flue gas from an oxyfuel-fired coal power station will be wet CO<sub>2</sub>, containing SO<sub>x</sub>, NO<sub>x</sub> and mercury. This CO<sub>2</sub> must be dried, compressed and purified before being sent for sequestration or used for EOR. In the process of compressing the CO<sub>2</sub> conditions are created for the reaction of SO<sub>2</sub> with NO<sub>2</sub> to form sulphuric acid, given enough residence time. Further, once all of the SO<sub>2</sub> has reacted, NO<sub>2</sub> will be converted to nitric acid by the addition of water. All of the SO<sub>x</sub> are removed and around 90% of the NO<sub>x</sub>, before drying, removal of inerts, and compression to 100-200 bar. Removing inerts involves cooling the raw CO<sub>2</sub> to a temperature close to its triple point where inerts are removed in the gas phase. This leads to CO<sub>2</sub> purities of around 95-98%. Modifications to this cycle allow purities of CO<sub>2</sub> greater than 99.9mol% with ppm levels of oxygen, a key impurity in the required purity of CO<sub>2</sub> for EOR.

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<sup>1</sup> Power includes adiabatic compression as discussed, without credit for steam system feedwater heating, so numbers may appear high compared to intercooled compression